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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER
FORM PT0-1390 (REV 11-98)		SPM-301-A
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/601374
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP99/00517	January 27, 1999	January 28, 1999
TITLE OF INVENTION SUBSTRATE FOR PACKAGING PERISHABLE GOODS OR FOR APPLICATION ONTO SAME AND METHOD FOR DETERMINING THE QUALITY OF SAID GOODS		
APPLICANT(S) FOR DO/EO/US DIETRICH HAARER, YOAV ETCHEN		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (unsigned) <input checked="" type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 		
Items 11. to 16. below concern document(s) or information included:		
<ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <ol style="list-style-type: none"> <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input checked="" type="checkbox"/> Other items or information: Associate Power of Attorney 		

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Associate Power of Attorney			

09/601374

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Our Reference: SPM-301-A

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Dietrich Haarer, Yoav Eichen
Serial Number: Unknown
Filing Date: July 28, 2000
Examiner/Art Group Unit: Unknown/Unknown
Title: SUBSTRATE FOR PACKAGING PERISHABLE
GOODS OR FOR APPLICATION ONTO SAME
AND METHOD FOR DETERMINING THE
QUALITY OF SAID GOODS

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, D.C. 20231
Box: Non-Fee

Sir:

If any charges or fees must be paid in connection with the following communication, they may be paid out of our Deposit Account No. 25-0115.

Prior to initial examination, please amend the above-identified patent application as indicated below.

In the claims:

Please amend the following claims as indicated.

In claim 3, line 1 delete "or 2".

In claim 4, line 1 delete "one of the preceding claims" and insert - -claim 1- -.

In claim 5, line 1 delete "one of the preceding claims" and insert - -claim 1- -.

6. (Amended) Substrate according to [one of claims] claim 4 [or 5], characterised in that in the general formula I and II, R₄ = NO₂ and 2 - 4 NO₂ groups are present.

In claim 7, line 1 delete "or 2".

In claim 8, line 1 delete "or 2".

In claim 9, line 1 delete "one of the preceding claims" and insert - -claim 1- -.

In claim 10, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 11, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 12, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 13, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 15, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 16, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 17, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 18, line 1 delete "one of the preceding claims" and insert - -claim 1--.

In claim 19, line 2 delete "one of claims" and insert - -claim- -.

In claim 19, line 2 delete "to 18".

In claim 21, line 1 delete "or 20".

22. (Amended) Process according to [one of claims] claim 19 [to 21], characterised in that the filter is applied after optically induced colouration.

23. (Amended) Process according to [one of claims] claim 19 [to 22], characterised in that the optically induced colouration of the reversible indicator is effected by UV or near UV light.

24. (Amended) Process according to [one of claims] claim 19 [to 23], characterised in that the optical activation of the time-temperature integrator is effected by irradiation on the side of the time-temperature integrator opposite the filter.

REMARKS

After entry of this amendment, claims 1-24 are pending in the application. Claims 3-13, 15-19 and 22-24 have been amended.

It is submitted that this Amendment has antecedent basis in the application as originally filed, including the specification, claims and drawings, and that this Amendment does not add any new subject matter to the application. Consideration of the application as amended is requested. It is submitted that this Amendment places the application in suitable condition for allowance; notice of which is requested.

If the Examiner feels that prosecution of the present application can be expedited by way of an Examiner's amendment, the Examiner is invited to contact the Applicant's attorney at the telephone number listed below.

Respectfully submitted,

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DPC/rlb

USPTO Patent and Trademark Office

09/601374

534 Rec'd PCT/PTC 28 JUL 2000
**Substrate for packaging of or attachment to
perishable products and process
for determination of quality thereof**

The invention relates to a substrate for packaging of or attachment to perishable products which are sensitive to aging or temperature, such as foodstuffs or medicaments, and a process for determination of quality thereof.

When using transitory materials, it is often desirable to determine the age and the current shelf status of the materials. If attachment of an expiry date to the packaging has been considered adequately beforehand, this procedure today is too imprecise and has too little security against falsification for a number of products. In particular the status of transitory products is usually not only a function of time, but also of further parameters, such as in particular the temperature.

United States patent 3 999 936 takes up this problem and proposes attaching an indicator showing the time-temperature previous history to the perishable products. The originally colourless indicator based on acetylene shows a characteristic, irreversible discolouration, depending on period of storage and storage temperature of the product, by means of which conclusions can be made on the quality of the stored perishable product.

However, its tedious handling stands in the way of further expansion of the process known from United States patent 3 999 946. Hence, the indicator must be stored at very low temperatures and in the dark until it is attached to the product to initially delay the onset of the actual required time-temperature effect initiated by indicator synthesis. The indicator reaction itself proceeds auto-catalytically and strongly non-linearly, which makes precise evaluation more difficult. The disadvantage is also that the indicator reaction is irreversible, so that use is excluded for multiple-use packages finding increasing expansion.

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Starting from this and further disadvantages of the state of the art, the object of the invention is to indicate a substrate for packaging of or attachment to perishable products, which permits determination of quality of the products, is simple to handle and furthermore can also be used several times. The object is also to provide a process for determination of quality which permits safe and precise determination for the shelf status of the perishable product.

This object is achieved by a substrate according to claim 1 and as regards process technology by claim 20. The sub-claims relate to preferred embodiments and further developments of the invention.

A substrate for packaging of or for attachment to products which are sensitive to aging and temperature, having a planar time-temperature integrator arranged in or on or below the substrate, allows a reliable determination of quality of perishable products if the time-temperature integrator contains at least one reversible indicator, which is embedded in a matrix and has photochromic properties on the basis of transfer reactions. Transfer reaction is generally understood to mean those reactions which take place during the change in the atomic characteristic activities, which involves the relocation of at least one atom. An example is the transfer of a hydrogen atom (or a proton or hydride). Here the above-mentioned species of a "donor" group is transferred to an "acceptor" group and thus forms a tautomeric compound. During transfer of other groups, isomeric or charged species may be formed during the transfer reaction.

On the basis of the photochromic properties, the indicator can be coloured in photo-induced manner by irradiating with photons of a certain energy range, wherein a time-dependent and temperature-dependent discolouration occurs following colouration. The required reversibility of the indicator reaction allows renewed photo-induced colouration after or during discolouration. Colouration of the indicator may be effected at a defined point in time, preferably for example immediately before or after production or packaging of the perishable material.

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In contrast to the indicator materials of the state of the art, the time-temperature clock can thus be started defined at a required point in time and does not begin to proceed irreversibly even at the point in time of indicator synthesis. In addition, according to the invention the colouration process is not considered, but the reverse reaction, that is discolouration.

The time-temperature integrator may be provided with a filter to avoid undesirable renewed coloration of the indicator after starting the time-temperature clock by filtering out certain wavelength ranges. In addition, a further, irreversible indicator may be arranged, for example next to or above the reversible indicator, to secure against falsification. The further indicator indicates with reversible colouration that the reversible indicator has been coloured again after production or packaging of the perishable goods.

The reversible indicator may be produced both as a solid, for example in the form of glasses or crystals, and in solution. Production is possible both as pure substance and at the same time with the matrix. Above all, crystalline indicators show adequately long discolouration times of typically one day and longer for conventional commercial applications. Amorphous indicators usually show discolouration times of less than one day. By selecting the synthesis conditions or varying the crystal growth processes, the discolouration times can be set specifically between almost instantaneous discolouration up to days, weeks or months.

Indicators having more than one characteristic time domain may also be produced. Such indicators may have, for example a phase transition, wherein the different phases show different discolouration behaviour. The simultaneous use of two or more indicators having different time domains is likewise possible.

The indicators are preferably embedded in a carrier matrix. The matrix term has a very broad meaning according to the invention, and includes, for example also the substrate. Hence, it is conceivable to incorporate the indicators directly in a region of the substrate.

The actual determination of quality of products which are sensitive to aging or temperature initially assumes photo-induced colouration of the reversible indicator. Colouration may take place before application of a filter or the irreversible indicator or from a side of the substrate opposite the filter. At a later point in time, the degree of time-related or temperature-related discolouration is then measured and the product quality is concluded therefrom. During evaluation with the aid of the human eye, it may be advantageous if a reference scale is arranged, for example next to or below the substrate, which assigns a certain quality grade, a certain point in time etc., to a certain degree of discolouration.

Further details and preferred embodiments of the invention can be seen from the figures and exemplary embodiments.

Figure 1 shows a skeletal structure of a photo-induced reversible indicator;

Figure 2 shows a further skeletal structure of a photo-induced reversible indicator;

Figure 3 shows examples of reversible indicators;

Figure 4 shows examples of proton transfer reactions;

Figure 5 shows an example of a methyl group transfer reaction;

Figure 6 shows an example of a halogen transfer reaction;

Figure 7 shows an indicator system having two characteristic time domains; and

Figure 8 shows a time-temperature integrator with reference scale in plan view.

The substrates of the invention are suitable for packaging of or attachment to perishable products, such as foodstuffs (for example frozen goods), medicaments, drugs, transplant

organs and transitory materials. The time-temperature indicator connected to the substrate may be designed to be planar or, for example in the form of a pattern or logo. Although all components can be recycled, disposal is in principle harmless, since no poisonous or pollutant materials have to be used.

The photochromic indicator reactions may be based, for example on reversible electron transfer or on the reversible transfer of a charged or uncharged hydrogen atom (proton, hydride) or a hydrogen isotope (deuterium, tritium). Transfer is preferably of protons, deuterons, halogen radical ions or simple chemical groups, such as methyl groups.

Figure 1 shows the skeletal structure of a reversible indicator.

The radicals are A₁ – A₅ preferably a carbon atom or heteroatom, such as for example N, S, O etc.; R₁ – R₄ is an atom, such as hydrogen or its isotopes or also Cl, F, Br atoms; or other substituents, such as for example alkyl groups, in particular methyl groups or aryl groups, in particular phenyl groups. R₅ is H, D or T or substituents, such as for example Cl, F, Br etc. or an alkyl group, in particular methyl group or an aryl group, in particular phenyl or pyridine. R₆ is H, D, T and B₁ – B₇ is a carbon atom or heteroatom, such as for example N, S, O etc.. R₁ – R₁₀ are preferably atoms, such as for example hydrogen atoms or their isotopes or one or more Cl, F, Br, amino groups or nitro groups etc. or one or more substituents, such as for example alkyl groups, in particular methyl or aryl groups, in particular phenyl. R₁₁ is a nitro group or a cyano group or a carboxylic acid group or a variant, such as for example an ester, amide, ketone or aldehyde group.

A₁ – A₅ is particularly preferably a carbon atom and R₁ – R₄ hydrogen (pyridine). The pyridine ring may also be part of an extended molecular system (quinoline, phenanthroline etc.), in addition, the variants preferably designated further As are replaced by N, such as for example pyrazine, pyridazine, pyrimidine, tetrazine, pentazine etc..

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The radical R₁₁ is at least one NO₂, NH₂ or CN group. It is preferable if an NO₂ group is present which forms an ortho-nitro phenyl group. Furthermore, the phenyl group may be part of a larger, extended molecular system. In addition, one or more carbon atoms of the phenyl ring may be replaced by heteroatoms.

A further suitable skeletal structure is shown in Figure 2. The phenanthroline group is essential here.

A₁ – A₁₂ thus denotes a carbon atom or heteroatom, such as for example N, S, O etc.. R₁ – R₇ an atom, such as hydrogen or its isotopes or Cl, F, B or other substituents, such as for example alkyl groups, in particular methyl or aryl groups, in particular phenyl. R₈ is H, D, T or a substituent, such as for example Cl, F, Br etc. or an alkyl group, in particular methyl or an aryl group, in particular phenyl or pyridine. R₉ = a nitro group or a cyano group or a carboxylic acid group or a variant, such as for example an ester, amide, ketone or aldehyde group. R₁₀ – R₁₃ is an atom, such as for example hydrogen or its isotopes or one or more Cl, F, Br, amino groups or nitro groups etc. or one or more substituents, such as for example alkyl groups, in particular methyl or aryl groups, in particular phenyl.

The phenanthroline group bonded to B₁ is essential.

The phenanthroline group may have different substituents R₁ – R₇, which are hydrogen in the simplest case, but which may also consist of methyl groups, phenyl groups. In addition, the phenanthroline group may be part of an extended molecular system (such as for example for quinoquinolines). Furthermore, one or more As of the phenanthroline molecule may be replaced by heteroatoms (for example nitrogen for azaphenanthroline etc.) Compounds having other heteroatoms are also suitable here.

It generally applies that different length discolouration times may be achieved depending on the type of photochemically induced transfer reaction and in particular depending on binding strength of the “acceptor” of the transferred species.

Figure 3 shows examples of indicators having the skeletal structure according to Figure 1, in each case having the associated typical discolouration times at a temperature of 298 K. Provided, where two times are indicated, they are systems which have two different phases.

Depending on application, a compound having optimised time-temperature behaviour may be used.

Examples of proton transfer reactions are sketched in Figure 4. The initially colourless indicator is thus irradiated with UV light or near UV light, whereupon a proton transfer and a thus concomitant indicator colouration takes place. This photo-induced proton transfer then proceeds back in the other direction as a function of time and temperature, so that the indicator is discoloured successively. Analogous reactions, based on the transfer of methyl groups or halogen radicals, are shown in Figure 5 and 6.

Figure 7 shows a system which has two crystalline phases and two different characteristic time domains. Phase transition from a first crystalline phase with long discolouration times to a second crystalline phase having a discolouration time which is shorter by a factor 10 is effected at a temperature of 318 K. Other phase transitions, for example crystal fusion, show similar properties.

Figure 8 shows the procedure for determination of quality with the aid of a time-temperature integrator 1. A printed reference scale 2, which permits an absolute determination of quality grades by means of the likewise printed assignment scale 3, is arranged above the time-temperature integrator 1. The time-temperature integrator is advantageously arranged on a light substrate to facilitate reading.

Both inorganic and organic materials, preferably those which are known from conventional layer and packaging techniques, are suitable as substrate materials. Polymers, glass, metals, paper, cardboard etc. may be mentioned by way of example. The

substrate may form at the same time the packaging material for the perishable products or be attached to the packaging material or directly to the product.

The reversible indicator is introduced either directly into the substrate material, wherein the substrate assumes the matrix function and is preferably arranged on or below the substrate in the form of an indicator-doped matrix. The reversible indicator may be embedded in the matrix in the form of small crystallites or in solid solution. The matrix is, for example a polymer (PVC, PMMA, PEO, etc.) or glass-like film. Indicator-doped matrices can also be produced by means of sol-gel techniques.

The irreversible photosensitive indicator intended as falsification security may be applied to the time-temperature integrator as a coating. For example pyrrole derivatives, such as 2-phenyl-di(2-pyrrole)methane, are suitable irreversible indicators. This material becomes irreversibly red if it is exposed to UV light.

After applying the irreversible indicator, a colour filter is arranged on the time-temperature integrator. Yellow filters, which are permeable only to light having typical wavelengths of over 430 nm, are suitable for UV-sensitive indicators.

The photo-induced charging of the time-temperature integrator is preferably effected before applying the irreversible indicator and the filter. Alternatively, the intention may also be to charge the time-temperature integrator from a substrate side not covered by a filter.

Some production examples for time-temperature integrators are illustrated in detail below:

Polymer films doped with 2-(2,4-dinitrobenzyl)pyridine:

100 mg of 2-(2,4-dinitrobenzyl)pyridine, α -DNBP, are dissolved in 50 ml of tetrahydrofuran (solution A). 330 mg of PVC (for example molecular weight 100,000)

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are dissolved in 50 ml of tetrahydrofuran and filtered (solution B). Solution A and solution B are mixed in a suitable container, the substance is cast into a thin film and the latter is dried in the dark at about 40°C. The film being formed is about 100 µm thick, transparent and it shows excellent mechanical and optical properties. The films may be produced in different shapes and thicknesses. The transparent doped film becomes coloured during activation (for example UV radiation) and is discoloured at a rate which is characteristic for the particular material selected, depending on the time and temperature. The system is reversible over many cycles.

Pure organic glasses of 2-(2,4-dinitrobenzyl)pyridine compounds:

3 mg of a glass-forming material, such as for example derivatives of 2-(2,4-dinitrobenzyl)pyridine (for example as heteroaryl-substituted material in 6 position) are melted between 2 transparent glasses or between two flexible films, and after melting, quenched, for example by cooling in liquid nitrogen. The glass being formed is fully transparent and has variable thickness. The glass is stable for long periods and at very different temperatures.

Polymer "pellets" doped with 2-(2,4-dinitrobenzyl)pyridine:

2 mg of 2-(2,4-dinitrobenzyl)pyridine, α -DNBP, are ground to a very fine powder. In order to determine the gradation of grinding, the following tests may be undertaken:

1. Irradiation of the crystals (350 nm < λ < 400 nm)
2. Grinding of the crystals
3. Irradiation of the crystals (350 nm < λ < 400 nm)
4. Grinding of the crystals
5. If the colour of the powder remains the same, the grinding process is interrupted.

The size of the crystals is then just a few µm. The ground dust is mixed with 100 mg of a suitable matrix, such as for example PS, PED etc. and placed in a press. The chamber

with the material is then evacuated and exposed to a pressure of 15-20 kbar (for about 30 minutes). The result is a 1-2 mm thick tablet which appears white. The thin tablet becomes deep blue on irradiation by appropriate light (preferably UV). The tablet is then discoloured again as a consequence of time and temperature. The system is reversible and may, if required, be cycled many times.

All above-mentioned samples are not sensitive to light if they are coated with an inexpensive, yellow polymer or cellophane film. An indicator, which may also be used in daylight, may be produced in this manner.

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PATENT CLAIMS

1. Substrate for packaging of or for attachment to products which are sensitive to aging and temperature, having a time-temperature integrator arranged in the region of the substrate, characterised in that the time-temperature integrator contains a matrix and at least one reversible indicator embedded therein, which has photochromic properties on the basis of transfer reactions.
2. Substrate according to claim 1, characterised in that the substrate is a packaging material.
3. Substrate according to claim 1 or 2, characterised in that the transfer reactions are based on the transfer of charged or uncharged hydrogen atoms or hydrogen isotopes.
4. Substrate according to one of the preceding claims, characterised in that the reversible indicator has a skeletal structure according to the general formula I:

(Formula page 2 of claims)

wherein A₁ - A₅ = carbon atom and/or a heteroatom, such as for example N, S, O

$R_1 - R_4$ = hydrogen atom and/or an isotope thereof, and/or Cl, F, Br or a substituent, such as for example alkyl groups, in particular methyl groups or aryl groups, in particular phenyl groups.

R_5 = H, D or T or a substituent, such as for example Cl, F, Br or an alkyl group, in particular methyl group or an aryl group, in particular phenyl or pyridine, and

$$R_6 = H, D, T$$

$B_1 - B_7$ = carbon atom and/or a heteroatom, such as for example N, S, O.

$R_1 - R_{10}$ = hydrogen atom and/or an isotope thereof, and/or one or more Cl, F, Br, amino groups or nitro groups or one or more substituents, such as for example alkyl groups, in particular methyl or aryl groups, in particular phenyl, and

R_{11} = nitro group or a cyano group or a carboxylic acid group or a variant, such as for example an ester, amide, ketone or aldehyde group.

5. Substrate according to one of the preceding claims, characterised in that the reversible indicator has a skeletal structure according to the general formula II:

(Formula page 3 of claims)

- wherein $A_1 - A_{12}$ = carbon atom and/or a heteroatom, such as for example N, S, O.
- $R_1 - R_7$ = hydrogen atom and/or an isotope thereof, and/ or Cl, F, B or other substituents, such as for example alkyl groups, in particular methyl or aryl groups, in particular phenyl.
- R_8 = H, D, T or a substituent, such as for example Cl, F, Br or an alkyl group, in particular methyl or an aryl group, in particular phenyl or pyridine.
- R_9 = H, D, T
- $B_1 - B_7$ = carbon atom and/or heteroatom, such as for example N, S, O.

$R_{10} - R_{13}$ = hydrogen atom and/or an isotope thereof, and/or one or more Cl, F, Br, amino groups or nitro groups, or one or more substituents, such as alkyl groups, in particular methyl or aryl groups, in particular phenyl.

R_{14} = nitro group or a cyano group or a carboxylic acid group or a variant, such as for example an ester, amide, ketone or aldehyde group.

6. Substrate according to one of claims 4 or 5, characterised in that in the general formula I and II, $R_4 = NO_2$ and 2 – 4 NO_2 groups are present.
7. Substrate according to claim 1 or 2, characterised in that the transfer reactions are based on large, charged or uncharged groups.
8. Substrate according to claim 1 or 2, characterised in that the transfer reactions are based on a charged or uncharged halogen atom.
9. Substrate according to one of the preceding claims, characterised in that the reversible indicator has more than one characteristic time domain.
10. Substrate according to one of the preceding claims, characterised in that at least two reversible indicators having different characteristic time domains are embedded in the matrix.
11. Substrate according to one of the preceding claims, characterised in that the reversible indicator has photo-induced colouration.
12. Substrate according to one of the preceding claims, characterised in that at least one irreversible indicator having photochromic properties is arranged in the region of the reversible indicator.

13. Substrate according to one of the preceding claims, characterised in that the time-temperature integrator has a filter which is impermeable to light, which effects photo-induced colouration of the reversible indicator.
14. Substrate according to claim 13, characterised in that the filter is impermeable in the wavelength range of a wavelength preferably below 430 nm.
15. Substrate according to one of the preceding claims, characterised in that the substrate includes a reference scale arranged in the region of the time-temperature integrator.
16. Substrate according to one of the preceding claims, characterised in that the matrix is a polymer film.
17. Substrate according to one of the preceding claims, characterised in that the substrate is a polymer film.
18. Substrate according to one of the preceding claims, characterised in that a substrate region forms the matrix for the reversible indicator.
19. Process for determination of quality of products which are sensitive to aging and temperature and are provided with a substrate according to one of claims 1 to 18, containing the steps:
- a) photo-induced colouration of the reversible indicator; and
 - b) determination of the degree of time-related or temperature-related discolouration and the quality of the product taking into account the degree of discolouration.
- 00016004727660

20. Process according to claim 19, characterised in that the determination of the quality of the product is effected by evaluating the degree of discolouration with the aid of the reference scale.
21. Process according to claim 19 or 20, characterised in that the irreversible indicator is applied after optically induced colouration of the reversible indicator.
22. Process according to one of claims 19 to 21, characterised in that the filter is applied after optically induced colouration.
23. Process according to one of claims 19 to 22, characterised in that the optically induced colouration of the reversible indicator is effected by UV or near UV light.
24. Process according to one of claims 19 to 23, characterised in that the optical activation of the time-temperature integrator is effected by irradiation of the side of the time-temperature integrator opposite the filter.

00000000000000000000000000000000

Abstract

The invention relates to a substrate for packaging of or for attachment to products which are sensitive to aging and temperature, having a planar time-temperature integrator comprising a matrix and at least one reversible indicator embedded therein, which has photochromic properties on the basis of transfer reactions, arranged in the region of the substrate.

03/03/2014 11:42:27 PM

HAARER, Dietrich, Dr.

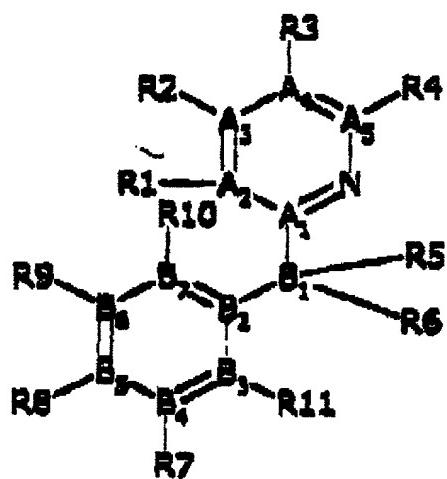
Patent claim 1

Substrate for packaging of or for attachment to products which are sensitive to aging and temperature, having a time-temperature integrator arranged in the region of the substrate, characterised in that the time-temperature integrator contains a matrix and at least one reversible and re-chargeable indicator embedded therein, which has photochromic properties on the basis of transfer reactions.

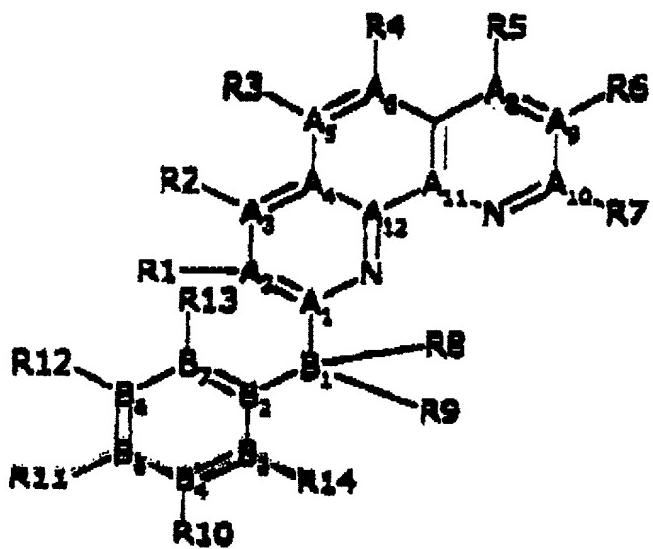
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117

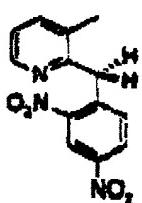
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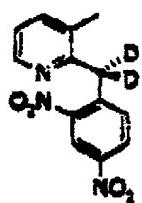
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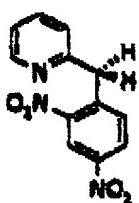


Crystal (T=298K)

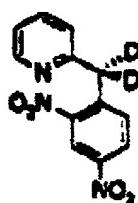


Crystal (T=298K)
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 $t_2 = 24200 \text{ s}$

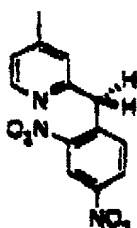
$t_1 = 36000 \text{ s}$
 $t_2 = 1700000 \text{ s}$



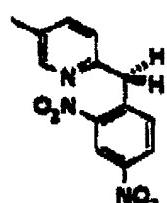
Crystal (T=298K)



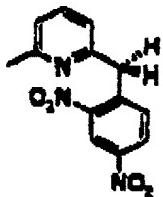
$t = 16000 \text{ s}$ Crystal (T=298K) $t = 73000 \text{ s}$



Crystal (T=298K)



$t = 23200 \text{ s}$ Crystal (T=298K) $t = 427 \text{ s}$



Crystal (T=298K) $t = 427 \text{ s}$

Figure 3

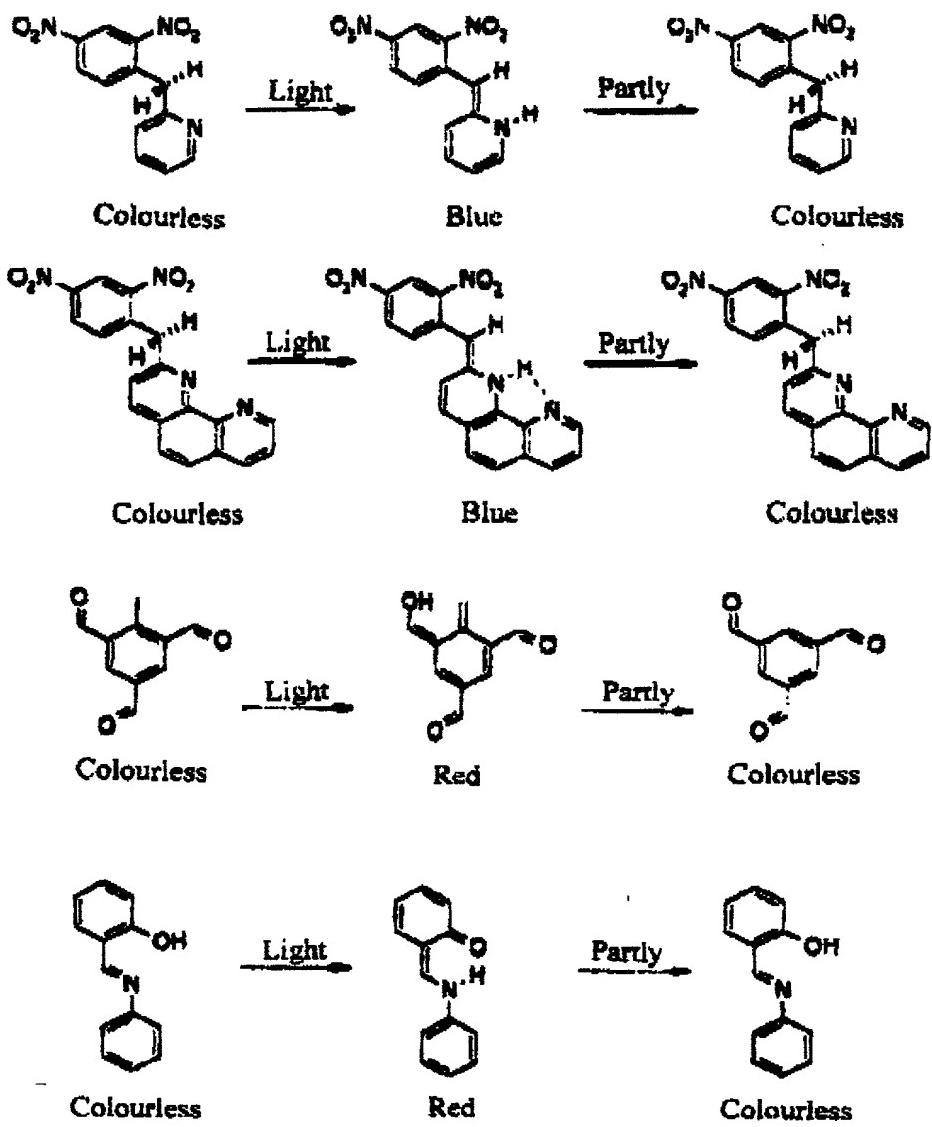


Figure 4

417

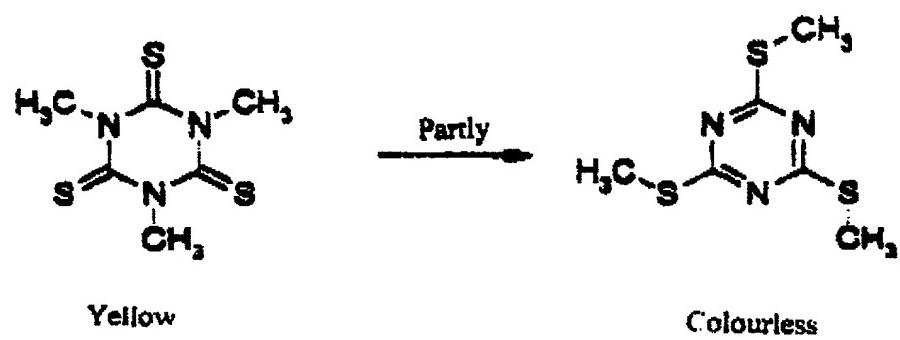


Figure 5

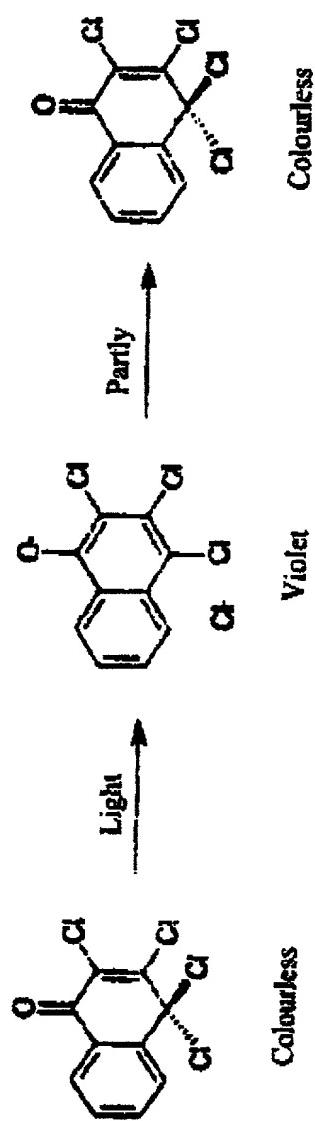


Figure 6

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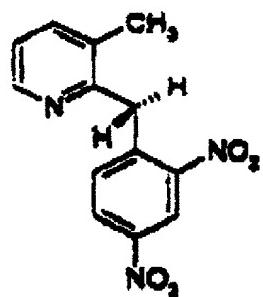
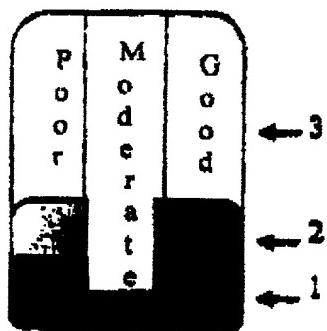
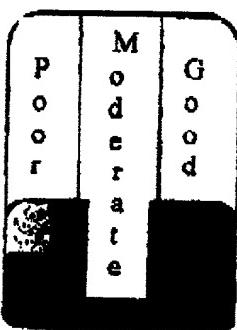


Figure 7

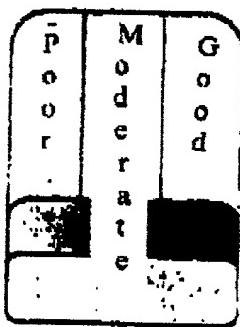
7/7



"Good"



"Moderate"



"Poor"

Figure 8

Our Reference: SPM-301-A

**COMBINED DECLARATION, POWER OF ATTORNEY AND
VERIFIED STATEMENT CLAIMING SMALL ENTITY STATUS**

DECLARATION:

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint Inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**SUBSTRATE FOR PACKAGING PERISHABLE GOODS OR FOR APPLICATION ONTO SAME AND METHOD FOR
DETERMINING THE QUALITY OF SAID GOODS**

the specification of which (check only one item below):

[] is attached hereto.

[] was filed as United States application Serial No. _____ on _____, and was amended on or through _____ (if applicable).

[X] was filed as PCT international application Number PCT/EP99/00517 on Jan 27, 1999, and was amended under PCT Article 19 on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate or §365(a) of any PCT international application(s) which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT international application(s) having a filing date before that of the application on which priority is claimed:

Prior Foreign/PCT Application(s) and any Priority Claims Under 35 U.S.C. §119:	Priority Claimed
--	------------------

<u>PCT/EP99/00517</u>	<u>Germany</u>	<u>27/1/1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Mo/Yr Filed)	Yes	No
<u>19803208.0</u>	<u>Germany</u>	<u>28/1/1998</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Mo/Yr Filed)	Yes	No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

<u>(Application Number)</u>	<u>(Filing Date)</u>
-----------------------------	----------------------

<u>(Application Number)</u>	<u>(Filing Date)</u>
-----------------------------	----------------------

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or §365(c) of any PCT international application(s) designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

Prior U. S. Application(s) or PCT International Application(s) Designating the U.S. for Benefit Under 35 U.S.C. §120:

<u>(Application Number)</u>	<u>(Filing Date)</u>	<u>(Status: patented, pending, abandoned)</u>
-----------------------------	----------------------	---

<u>(Application Number)</u>	<u>(Filing Date)</u>	<u>(Status: patented, pending, abandoned)</u>
-----------------------------	----------------------	---

POWER OF ATTORNEY:

I hereby appoint the following attorney(s) and/or agent(s) Thomas N. Young, Patent Office Registration No. 20985, Andrew R. Basile, Patent Office Registration No. 24753, William M. Hanlon, Jr., Patent Office Registration No. 28422, Marshall G. MacFarlane, Patent Office Registration No. 30403, Donald L. Wood, Patent Office Registration No. 20014, Thomas D. Helmholdt, Patent Office Registration No. 33181, Todd L. Moore, Patent Office Registration No. 36874 and Jason J. Young, Patent Office Registration No. 34048 as my attorney(s) and/or agent(s), to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith.

Send all correspondence to: Andrew R. Basile
Young & Basile, P.C.
3001 West Big Beaver Road, Suite 624
Troy, Michigan 48084
Phone: (248) 649-3333

VERIFIED STATEMENT:

I hereby declare that I qualify as an independent inventor as defined in 37 CFR §1.9(c) for purposes of paying reduced fees under §41(a) and (b) of Title 35, United States Code, to the Patent and Trademark Office with regard to the above-entitled invention described in the specification.

I have not assigned, granted, conveyed or licensed and am under no obligation under contract or law to assign, grant, convey or license any rights in the invention to any person who could not be classified as an independent inventor under 37 CFR §1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 CFR §1.9(d) or a nonprofit organization under 37 CFR §1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed or licensed or am under an obligation under contract or law to assign, grant, convey or license any rights in the invention is listed below:

- no such person, concern or organization;
 person, concerns or organizations listed below

FULL NAME _____

ADDRESS _____
 INDIVIDUAL SMALL BUSINESS CONCERN NONPROFIT ORGANIZATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor Dietrich Haaser

Inventor's Signature Dietrich Haaser

Date July 25 2008 Citizenship German

Residence Germany

Post Office Address Hanweg 30, D-95448, Bayreuth, Germany 604

Full name of second joint inventor, if any Yoav Eichen

Inventor's Signature X

Date _____ Citizenship Israel

Residence Israel

Post Office Address Avigavil Street 20, 32000 Haifa, Israel

Additional inventors are being named on separately numbered sheets attached hereto.

Our Reference: SPM-301-A

COMBINED DECLARATION, POWER OF ATTORNEY AND
VERIFIED STATEMENT CLAIMING SMALL ENTITY STATUS**DECLARATION:**

As a below named Inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SUBSTRATE FOR PACKAGING PERISHABLE GOODS OR FOR APPLICATION ONTO SAME AND METHOD FOR DETERMINING THE QUALITY OF SAID GOODS

the specification of which (check only one item below):

 is attached hereto. was filed as United States application Serial No. _____ on _____, and was amended on or through _____ (if applicable). was filed as PCT International application Number PCT/EP99/00517 on Jan 27, 1999, and was amended under PCT Article 19 on _____ (if applicable).

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PCT/EP99/00517	Germany	27/1/1999	(X)	[]
(Number)	(Country)	(Day/Mo/Yr Filed)	Yes	No
19803208.0	Germany	28/1/1998	(X)	[]
(Number)	(Country)	(Day/Mo/Yr Filed)	Yes	No

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(Application Number)	(Filing Date)

(Application Number)	(Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or §365(c) of any PCT international application(s) designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

Prior U. S. Application(s) or PCT International Application(s) Designating the U.S. for Benefit Under 35 U.S.C. §120:

(Application Number)	(Filing Date)	(Status: patented, pending, abandoned)

POWER OF ATTORNEY:

I hereby appoint the following attorney(s) and/or agent(s) Thomas N. Young, Patent Office Registration No. 20985, Andrew R. Basile, Patent Office Registration No. 24753, William M. Hanlon, Jr., Patent Office Registration No. 28422, Marshall G. MacFarlane, Patent Office Registration No. 30403, Donald L. Wood, Patent Office Registration No. 20014, Thomas D. Helmholdt, Patent Office Registration No. 33181, Todd L. Moore, Patent Office Registration No. 36874 and Jason J. Young, Patent Office Registration No. 34048 as my attorney(s) and/or agent(s), to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith.

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Young & Basile, P.C.
3001 West Big Beaver Road, Suite 824
Troy, Michigan 48084
Phone: (248) 649-3333

VERIFIED STATEMENT:

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I have not assigned, granted, conveyed or licensed and am under no obligation under contract or law to assign, grant, convey or license any rights in the invention to any person who could not be classified as an independent inventor under 37 CFR §1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 CFR §1.9(d) or a nonprofit organization under 37 CFR §1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed or licensed or am under an obligation under contract or law to assign, grant, convey or license any rights in the invention is listed below:

- no such person, concern or organization;
 person, concerns or organizations listed below

FULL NAME _____

ADDRESS _____
INDIVIDUAL SMALL BUSINESS CONCERN NONPROFIT ORGANIZATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor Dietrich Haerer _____

Inventor's Signature X _____

Date _____ Citizenship German _____

Residence Germany _____

Post Office Address Harweg 30, D-95448 Bayreuth, Germany _____

Full name of second joint inventor, if any Yaav Eichen _____

Inventor's Signature X Eichen-Yaav _____

Date 15-08-00 Citizenship Israel _____

Residence Israel _____

Post Office Address Avigayil Street 20, 32000 Haifa, Israel _____

Additional inventors are being named on separately numbered sheets attached hereto.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Dietrich Haarer, Yoav Eichen
Serial Number: Unknown
Filing Date: July 28, 2000
Examiner/Art Group Unit: Unknown/Unknown
Title: SUBSTRATE FOR PACKAGING
PERISHABLE GOODS OR FOR
APPLICATION ONTO SAME AND
METHOD FOR DETERMINING THE
QUALITY OF SAID GOODS

ASSOCIATE POWER OF ATTORNEY

Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

The attorney of record:

Andrew R. Basile, Registration No. 24753

hereby grant an associate power of attorney(s)/agent(s) in the above-identified case
to:

Darlene P. Condra, Registration No. 37113

All correspondence in this matter should continue to be sent to:

Andrew R. Basile
YOUNG & BASILE, P.C.
3001 West Big Beaver, Suite 624
Troy, MI 48084-3107

Respectfully submitted,

YOUNG & BASILE, P.C.



Andrew R. Basile
Attorney for Applicant(s)
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3001 West Big Beaver Rd., Suite 624
Troy, Michigan 48084-3107
Dated: July 26, 2000
ARB/rhb